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EMULSIFIED WATER/HYDROCARBONS FUEL, ITS PREPARATION AND ITS USES

The present invention relates to a fuel comprising an emulsion of water and liquid hydrocarbons, intended to be used in heat engines and thermal machines. More precisely, the present invention relates to an emulsified water/hydrocarbons fuel that has improved high-temperature stability.

For many years, most of the oil companies have been working on the development of fuels (and motor fuels in particular) containing substitutes for hydrocarbons of petroleum origin, for reasons of economy of hydrocarbons and limitation of pollution. Thus, water very soon appeared as a particularly interesting partial substitute, provided it is maintained in stable emulsion with the hydrocarbons.

Thus, fuels have appeared on the market that comprise a mixture generally containing at least 5 wt.% of water and hydrocarbons, maintained as an emulsion by using special compositions of surfactant additives (or emulsifying systems). Relative to a conventional motor fuel consisting of hydrocarbons exclusively, during combustion in a diesel engine these fuels make it possible to reduce the emissions of pollutants such as, in particular, nitrogen oxides, carbon monoxide, particulates and unburnt hydrocarbons.

Thus, patent EP 630,398 describes an emulsified fuel based on a hydrocarbon fuel and water, in which the emulsifying system comprises a combination of three additives: sorbitan oleate (preferably sorbitan sesquioleate), polyalkylene glycol (preferably polyethylene glycol) and alkylphenol ethoxylate (preferably nonylphenol ethoxylate).

Patent EP 888,421 describes a fuel based on an emulsion of water in at least one hydrocarbon, and containing an emulsifying system comprising at least one

ester of sorbitol (preferably selected from the oleates of sorbitan), at least one fatty acid ester preferably selected from the oleates and/or the stearates and/or the ricinoleates of polyethylene glycol, and at least one polyalkoxylated alkylphenol preferably selected from the polyethoxylated nonylphenols and/or octylphenols.

Application WO 01/48123 proposes improving the thermal stability of said emulsified fuels, so as to permit the storage and use of the fuel over a wide temperature range, from -10°C to 70°C. This improvement is obtained by using an emulsifying system comprising at least one ester of sorbitol (preferably sorbitan sesquioleate), at least one polyalkoxylated fatty acid ester (preferably selected from the oleates, stearates and ricinoleates of polyethylene glycol), and at least one polyalkoxylated branched hydrocarbon compound preferably selected from the iso-, di- and trialkylated alcohols, preferably the isotridecyl alcohols containing from 3 to 10 ethoxylated groups.

Patent US 6,371,998 describes a liquid hydrocarbon fuel in which water-containing lipid vesicles have been incorporated. These lipid vesicles are constituted, for example, of 4 wt.% of alcohol polyoxyethylene-10-stearate, 7.2 wt.% of glycerol distearate, 5 wt.% of soya methyl ester, 5 wt.% of sorbitan sesquioleate and 78.8 wt.% of water.

Finally, patent application WO 01/51593 recommends, for improving the thermal stability over a wide temperature range (-20 to +50°C) of a fuel based on an emulsion of water and liquid hydrocarbons, using a polymeric emulsifier that can be obtained by reaction between a functionalized polyolefin oligomer and a polyoxyalkylene. That application also describes, for comparison, emulsifying systems comprising 87 wt.% of sorbitan monooleate, 3 wt.% of sorbitan trioleate, and 10 wt.% of castor oil ethoxylated with 10 moles of ethylene oxide.

However, the emulsified fuels described in the prior art prove to have insufficient high-temperature stability. In fact, the aqueous and hydrocarbon phases tend to separate quickly when the fuel is held at elevated temperatures, above 60°C, for several hours. Notably, this makes the use of these emulsified fuels incompatible with the new engine technologies, such as for example diesel engines equipped with pump-based direct injection systems. In these injection systems the fuel is submitted to temperatures generally above 70°C and, when the engine is stopped, the emulsion that still remains in the supply system tends to undergo phase separation, especially in the injector pump. This phenomenon causes many problems, including considerable difficulty in restarting the vehicle.

To solve this problem, the present invention proposes an emulsified fuel based on hydrocarbons and water, which has improved high-temperature stability relative to the emulsified fuels known in the prior art, without degradation of the other properties.

In fact, the Applicant discovered that the high-temperature stability of said emulsions could be improved considerably by using a special emulsifying system, comprising at least two surfactant additives.

With this aim, the present invention relates to an emulsified fuel containing a major proportion (typically at least 80%, advantageously at least 90%, more particularly at least 95% by weight) of an emulsion of water and liquid hydrocarbons with a water/hydrocarbon weight ratio ranging from 5/95 to 35/65. Said fuel is characterized in that it contains an emulsifying system comprising at least 15 wt.% of a fatty acid ester and (poly)oxyalkylated polyol, and of at least one member of the group comprising the esters of fatty acid and of sorbitan and the products of condensation of a succinic acid or anhydride with at least one amine, polyamine, fatty acid, (poly)oxyalkylated fatty acid, alcohol,

(poly)oxyalkylated alcohol and mixtures of said compounds.

Relative to the known emulsified fuels, the fuel according to the present invention has excellent thermal stability, permitting its storage and use both at cold or ambient temperature and at elevated temperatures, of the order of 75°C. Notably this makes its use perfectly compatible with the new engine technologies such as direct injection.

For the emulsified fuel according to the invention to remain stable over time, including at elevated temperature (i.e. for the water droplets to remain dispersed finely and uniformly in the hydrocarbon phase, and avoiding their coalescence leading eventually to separation of the aqueous phase and the organic phase), it contains an emulsifying system comprising at least two compounds, either at least two types of esters, or an ester of fatty acid and of (poly)oxyalkylated polyol and a product of condensation of a succinic acid or anhydride with at least one amine, polyamine, fatty acid, (poly)oxyalkylated fatty acid, alcohol, (poly)oxyalkylated alcohol.

The ester of fatty acid and of sorbitan, called sorbitan ester hereinafter, is constituted of an ester of fatty acid and of sorbitan or of a mixture of said esters. The term sorbitan, familiar to a person skilled in the art, denotes a cyclic tetraol which is an anhydride of sorbitol and can be obtained by dehydration of the latter. Tetraol denotes a polyol containing 4 hydroxyl groups. Sorbitan is generally present in chemical equilibrium with sorbitol.

Said sorbitan ester can comprise one or more monoesters, one or more polyesters, or a mixture of monoesters and polyesters. It can be obtained for example by esterification of one or more fatty acids and of sorbitan. The fatty acids included in the composition of the sorbitan ester, which may be linear or branched, saturated or unsaturated, advantageously contain from 6

to 22 carbon atoms, and preferably from 12 to 18 carbon atoms. For example, and nonlimitatively, said fatty acids can be selected from lauric, palmitic, stearic, oleic, linoleic, linolenic acids and mixtures thereof.

Preferably, said sorbitan ester contains at least one sorbitan oleate. Examples of suitable sorbitan oleates are sorbitan monooleate, sorbitan dioleate, sorbitan trioleate, sorbitan tetraoleate, sorbitan sesquioleate. Particularly preferably, said sorbitan ester comprises at least one ester selected from sorbitan monooleate and sorbitan sesquioleate.

The ester of fatty acid and of (poly)oxyalkylated polyol hereinafter designated polyol ester can comprise monoesters, polyesters or a mixture of monoesters and polyesters. In the case of polyesters, the fatty acids included in the composition of each of the ester molecules may be identical or different. Moreover, they may be different from one ester molecule to another so that it is a case of a mixture of polyesters.

By polyol we mean alcohols containing from 2 to 5 hydroxyl groups, preferably alkylene glycols, glycerol, pentaerythritol, their alkylated derivatives and their mixtures.

The fatty acids included in the composition of said polyol ester may be linear or branched, saturated or unsaturated, and advantageously contain from 6 to 22 carbon atoms, and preferably from 12 to 18 carbon atoms. Preferably, they are selected from the fatty acids that are naturally present, in free or esterified form, in vegetable and/or animal oils, such as for example, and nonlimitatively, lauric, palmitic, stearic, oleic, linoleic, linolenic acids, and mixtures thereof.

The polyoxyalkyl groups present in the polyol ester are a chain of identical or different oxyalkyl units, each oxyalkyl unit advantageously containing from 1 to 5 carbon atoms, preferably from 1 to 4 carbon atoms. Preferably, the polyoxyalkyl groups comprise ethoxy

units. Preferably, the polyoxyalkyl groups comprise at least one polyethoxy group.

The average number of moles of oxyalkyl units per mole of ester (or oxyalkylation number) is advantageously between 3 and 50, and preferably between 10 and 35, in particular when the polyol is glycerol.

Preferably, the polyol ester is constituted completely or partially of a triester of fatty acid(s) and of polyoxyalkylated glycerol or a mixture of said triesters. More preferably, it is constituted completely or partially of a triester of fatty acid(s) and of polyethoxylated glycerol or a mixture of said triesters.

Said polyol ester can be obtained for example by polyoxyalkylation of an ester or of a mixture of esters of fatty acid and of the polyol or alternatively by esterification of one or more fatty acids and of one or more polyoxyalkylated derivatives of the polyol.

Said polyol ester is advantageously obtained by oxyalkylation of vegetable and/or animal oil. Thus, according to a preferred embodiment, the polyol ester is constituted completely or partially of oxyalkylated vegetable and/or animal oil. Such a product comprises triesters of fatty acids and of polyoxyalkylated polyol (preferably glycerol), generally mixed with monoesters and/or diesters of fatty acids and of (poly)oxyalkylated polyol (preferably glycerol). Said oil can if necessary have undergone a purification treatment, before and/or after its oxyalkylation. We may mention, as suitable vegetable oil, among others: colza oil, soya oil, castor oil, sunflower oil, palm oil, oils extracted from resinous trees and the mixtures of said oils. We may mention, as suitable animal oil: yellow grease, tallow, poultry fats.

According to a particularly preferred embodiment, the polyol ester is constituted completely or partially of ethoxylated vegetable oil.

According to another preferred embodiment, the polyol ester is a diester of polyalkoxylated alkylene glycol

and more particularly the dioleate of polyethoxylated ethylene glycol, notably with molecular weight between 200 and 1000.

Said polyol ester is advantageously present in the emulsified fuel according to the invention at a content in the range from 0.5 to 5 wt.%, preferably from 0.5 to 2 wt.%.

In a first embodiment of the invention, the emulsifying system comprises from 15 to 100 wt.% of at least one polyol ester, and of at least one member of the group comprising the sorbitan ester and the products of condensation of a succinic acid or anhydride with at least one amine, polyamine, fatty acid, (poly)oxyalkylated fatty acid, alcohol, (poly)oxyalkylated alcohol and mixtures of said compounds.

More particularly, the emulsifying system according to the invention contains from 15 to 100 wt.% of at least one sorbitan ester combined with at least one polyol ester, according to a weight ratio of sorbitan ester to polyol ester that varies from 20/80 to 80/20 inclusive, preferably from 40/60 to 60/40 inclusive. Even more preferably, the amounts by weight of each of the two types of esters are roughly equal (45/55 to 55/45).

The sorbitan ester is advantageously present in the emulsified fuel according to the invention at a content ranging from 0.5 to 5 wt.%, preferably from 0.5 to 2 wt.%.

According to a particularly advantageous embodiment, the emulsifying system included in the composition of the emulsified fuel according to the invention also comprises, in addition to the two types of esters, at least one alcohol containing from 3 to 22 carbon atoms, and preferably from 6 to 12 carbon atoms. Said alcohol, which is advantageously a monohydric alcohol, may be linear or branched, saturated or unsaturated. Preferably it comprises at least one saturated branched alcohol. Examples of particularly suitable alcohols include the

ethyl hexanols (for example 2-ethyl hexanol), isopropanol, tert.-butanol, isopentanol, isotridecanol, fatty alcohols (i.e. containing from 12 to 22 carbon atoms).

The emulsified fuel according to the invention then contains advantageously from 0.1 to 5 wt.% of said alcohol, preferably from 0.3 to 2%, even more preferably from 0.5 to 1 wt.%.

The presence of said alcohol in the emulsifying system of the fuel according to the invention offers various advantages. On the one hand, this alcohol performs the role of co-surfactant with respect to said first and second esters, i.e. it facilitates and reinforces the emulsifying power of the latter. Moreover, it makes it possible to improve the uniformity in size of the water droplets: the latter are of a more uniform size (more monodisperse distribution) and smaller. The presence of large droplets is thus avoided, which has the immediate effect of improving the fuel's resistance to sedimentation (the phenomenon of accumulation of the water droplets at the bottom of the fuel, which occurs more quickly as the proportion of large droplets increases).

According to another embodiment that is also particularly advantageous, the emulsifying system included in the composition of the emulsified fuel according to the invention also comprises from 0 to 85 wt.% of at least one compound that is the product of condensation of a succinic acid or anhydride with at least one amine, polyamine, fatty acid, (poly)oxyalkylated fatty acid, alcohol, (poly)oxyalkylated alcohol and mixtures of said compounds, called condensation product hereinafter. Preferably, the product of condensation of at least one succinic anhydride with at least one polyamine is used.

The succinic acid or anhydride is advantageously substituted by a hydrocarbon radical which is preferably a polymeric radical, for example a polyisobutyl radical.

The presence of such a compound in the emulsifying system of the fuel according to the invention offers various advantages. On the one hand, it makes it possible to improve the uniformity of size of the water droplets. On the other hand it promotes compatibility of the emulsified fuel according to the invention with conventional fuels constituted entirely of hydrocarbons, so that these two types of fuels become interchangeable. It thus becomes possible, in a vehicle usually operating with a conventional hydrocarbon fuel, to fill the fuel tank with the emulsified fuel according to the invention without having to purge the fuel distribution system, and vice versa.

In another preferred form of the invention, the emulsifying system contains from 15 to 85 wt.% of at least one polyol ester and from 85 to 15% of at least one condensation product. This combination provides a notable increase in the excellent thermal stability of the emulsion containing esters, during its storage and use both at low temperature and at ambient temperature and finally at high temperatures, of the order of 75°C. The preferred emulsifying system in this form of the invention contains from 20 to 50 wt.% of at least one polyol ester and from 50 to 80% of at least one condensation product.

We would still be within the scope of the invention if this emulsifying system also has added to it at least one alcohol of the type described previously, i.e. a monohydric alcohol, which can be linear or branched, saturated or unsaturated, containing from 3 to 22 carbon atoms, and preferably from 6 to 12 carbon atoms.

In addition to the emulsifying agents described previously, the emulsified fuel according to the invention can contain many other emulsifying agents. A person skilled in the art will be perfectly capable of perfecting the formula of the emulsifying system according to the invention by adding other known emulsifiers, ionic or nonionic, synthetic or of natural

origin such as, for example, but nonlimitatively, compounds selected from the fatty acids, derivatives of fatty acids, fatty alcohols, ethoxylated aliphatic amines, esters of polyols, functionalized polymers and mixtures thereof.

The hydrocarbon phase of the emulsified fuel according to the invention can be constituted of any mixture of hydrocarbons. For this purpose it is possible to employ hydrocarbon fractions and mixtures of fractions of very diverse origin and nature. The choice is dictated essentially by the use for which the fuel is intended, by the availability of the various hydrocarbon fractions, and by economic considerations (cost of the fuel).

When the fuel is intended for use as fuel for heat engines, the hydrocarbon phase advantageously comprises one or more hydrocarbon fractions that occur in the composition of conventional motor fuels, and which can be selected notably from the gasoline fractions (distillation range generally within the range from 25 to 200°C), middle distillates such as for example the kerosene fractions (distillation range generally within the range from 160 to 240°C) and gas-oil fractions (distillation range generally within the range 160 to 400°C), biofuels, and mixtures of said fractions. These fractions can be obtained from oil refining, from agriculture (in the case of biofuels), or can be synthetic hydrocarbons (for example obtained by oligomerization of light olefins, or by Fischer-Tropsch synthesis from light hydrocarbons).

Biofuel denotes light alcohols (such as ethanol for example), oils of vegetable and/or animal origin and the esters of said oils. The hydrocarbon phase of the fuel according to the invention can thus advantageously contain from 0.1 to 60 wt.%, and preferably from 0.5 to 50 wt.% of biofuel. The preferred biofuels are the esters of alcohols containing from 1 to 4 carbon atoms and of fatty acids or of mixtures of fatty acids

containing from 16 to 22 carbon atoms. The biofuels that are particularly preferred are the methyl esters of vegetable oils such as for example, but nonlimitatively, soya, colza, sunflower, olive and palm oils.

When the fuel is intended for other uses, the hydrocarbon phase can comprise one or more of the aforementioned fractions for the fuels, and/or other fractions if required selected from the intermediate vacuum distillates (distillation range generally within the range 350 to 450°C), the heavy vacuum distillates (distillation range generally within the range 400 to 550°C), or even distillation residues, and generally from all the fractions used conventionally in fuels such as for example domestic fuel oil, fuel oils, petroleum residues, heating oils and mixtures of these fractions.

In the present description, all the distillation ranges are cited with reference to standard ASTM D 86 (distillation of petroleum products).

The fuel according to the invention is in the form of an emulsion of fine droplets of aqueous phase dispersed uniformly in the hydrocarbon phase. Advantageously, the average diameter of the droplets of aqueous phase is less than or equal to 5 μm, preferably to 3 μm, even more preferably to 1 μm. Preferably, the granulometric profile of the sizes of droplets is of the monodisperse type around a value of about 0.5 μm. The aforementioned values of average droplet size correspond to measurements carried out by laser granulometry.

The emulsified fuel according to the present invention can advantageously contain one or more biocidal agents, preferably in its aqueous phase. Said biocidal agent is preferably a bactericide and/or a fungicide. As nonlimiting examples of biocidal agents, we may mention isothiazolones and their chlorinated derivatives, benzalkonium chlorides, organic peroxides, isothiocyanates, thiocyanates, ammonium salts, salts of amines, and oxazolidines.

The emulsified fuel can also contain at least one antigelling agent. The following may be employed for example as antigelling agent: alcohols, glycols, derivatives of glycols or of alcohols, saline solutions.

It can also contain at least one antisoot agent. As examples of said agents, we may mention additives constituted of one or more metallic or alkaline-earth catalysts that promote the reactions of post-combustion of soot. The preferred catalysts are based on magnesium, calcium, barium, cerium, copper, iron or mixtures thereof. These catalytic promoters of soot destruction are easier to introduce in the emulsion than are generally compounds whose salts are soluble in water, and therefore in the aqueous phase of the emulsions according to the invention.

When the fuel is intended for use as fuel for heat engines, its sulfur content, determined according to standard NF M 07-100, is preferably less than or equal to 350 ppm, preferably less than or equal to 50 ppm, and even more preferably less than or equal to 10 ppm.

When the fuel is intended for use as fuel for thermal machines, its sulfur content, determined according to standard NF M 07-100, is preferably less than or equal to 1 wt.%, preferably less than or equal to 0.2 wt.%, and even more preferably less than or equal to 0.1 wt.%.

Regardless of its intended use, the content of polycyclic aromatic hydrocarbons of the fuel according to the invention, determined according to standard IP 391, is preferably less than or equal to 11 wt.%, more preferably less than or equal to 6 wt.%.

Moreover, for use as motor fuel, the emulsified fuel according to the invention preferably contains one or more other additives, which can be any additive usually employed in motor fuels, including for example but nonlimitatively:

- one or more cetane number improvers, such as for example inorganic or organic nitrates, for example ammonium nitrate, alkyl nitrates in which the alkyl

radical, linear or branched, saturated or unsaturated (preferably branched and saturated) contains from 3 to 20 and preferably from 5 to 15 carbon atoms (in particular 2-ethylhexyl nitrate), organic peroxides and in particular aryl peroxides in which the aryl group is a benzyl group or a substituted benzyl group (for example benzoyl peroxide), or alkyl peroxides in which the alkyl radical, linear or branched, saturated or unsaturated (preferably branched and saturated) contains from 2 to 20 and preferably from 2 to 15 carbon atoms (for example tert.-butyl peroxide);

- one or more filterability additives such as for example the copolymers ethylene/vinyl acetate (EVA), ethylene/vinyl propionate (EVP), ethylene/vinyl ethanoate (EVE), ethylene/methyl methacrylate (EMMA), ethylene/alkyl fumarate;

- one or more antifoaming additives, such as for example polysiloxanes, oxyalkylated polysiloxanes, amides of fatty acids;

- one or more detergent and/or anticorrosion additives, such as for example amines, succinimides, alkenyl succinimides, polyalkylamines, polyalkyl polyamines and polyetheramines;

- one or more lubricant or antiwear additives, such as for example fatty acids and their ester or amide derivatives, mono- and polycyclic carboxylic acids and their ester or amide derivatives;

- one or more cloud point additives, such as for example long-chain olefin / (meth)acrylic ester / maleimide terpolymers, derivatives of esters of fumaric or maleic acids;

- one or more antisedimentation additives, such as for example the copolymers (meth)acrylic acid / alkyl (meth)acrylate amidated by a polyamine, the polyamine alkylene succinimides, the derivatives of phthalamic acid and double-chain aliphatic amine;

- one or more polyfunctional additives for cold operation, such as for example polymers based on olefin and alkenyl nitrate.

The invention also relates to a method of preparation of an emulsified fuel as described previously, by preparing an emulsion of hydrocarbons and water, in the presence of the emulsifying system and some or all of other possible additives. All the conventional ways of preparing emulsions can be employed for this purpose.

It is advantageous to proceed by mixing some or all of the additives with one and/or the other of the phases, prior to forming the emulsion. For example, we may proceed in the way described in patent application WO 00/34419, by mixing the emulsifying system with the hydrocarbon phase, then passing the resulting mixture one or more times through an emulsor system supplied with the water necessary for forming the emulsion.

It is also advantageous to proceed in the way described in patent applications WO 00/034419 and WO 01/36569, by:

(a1) premixing the water and the emulsifying system, followed by dispersion in the hydrocarbon phase, or

(a2) simultaneous mixing of the hydrocarbon phase with the water and the emulsifying agent, then

(b) emulsion formation proper, by means of a suitable device, selected for example from rotor-stators, emulsors, static mixers, in-line turbine systems, ultrasonic shakers.

The emulsified fuel according to the present invention can be used in various applications. It can be used in particular as fuel for heat engines (notably gasoline or diesel engines), or for fuel cells. Its use as diesel engine fuel is particularly advantageous, in particular for the new diesel engines equipped with direct injection systems.

The fuel according to the invention can also be used as fuel for thermal machines such as for example industrial or domestic boilers, furnaces, turbines,

generators. A particularly advantageous use is as domestic fuel oil, i.e. as fuel for domestic boilers.

The invention also relates to a composition of emulsifying additives that can be used for example in emulsified water/hydrocarbons fuels in order to improve their high-temperature stability. This additive composition comprises 15 wt.% of at least one fatty acid ester of (poly)oxyalkylated polyol, and of at least one member of the group comprising the esters of fatty acid and of sorbitan and the products of condensation of a succinic acid or anhydride with at least one amine, polyamine, fatty acid, (poly)oxyalkylated fatty acid, alcohol, (poly)oxyalkylated alcohol.

This additive composition preferably contains from 15 to 100 wt.% of at least one glycerol ester, and of at least one member of the group comprising sorbitan ester and the products of condensation of a succinic acid or anhydride with at least one amine, polyamine, fatty acid, (poly)oxyalkylated fatty acid, alcohol, (poly)oxyalkylated alcohol and the mixtures of these compounds.

Preferably, it contains from 15 to 100 wt.% of at least one sorbitan ester combined with at least one polyol ester as described previously, in a weight ratio of sorbitan ester/polyol ester ranging from 20/80 to 80/20.

Preferably, the weight ratio of sorbitan ester/polyol ester varies from 40/60 to 60/40 inclusive. Even more preferably, the amounts by weight of each of the two types of esters are roughly equal (45/55 to 55/45).

Furthermore, advantageously the composition of emulsifying additives according to the invention also contains at least one alcohol containing from 3 to 22 carbon atoms, and preferably from 6 to 12 carbon atoms. Said alcohol, which is preferably a monohydric alcohol, may be linear or branched, saturated or unsaturated. It preferably contains at least one saturated branched alcohol.

The weight ratios of alcohol/polyol ester and alcohol/sorbitan ester are identical or different, and advantageously both are less than or equal to 1. Preferably, each of these ratios is between 0.2 and 1.

The composition of emulsifying additives according to the invention can moreover comprise from 0 to 85 wt.% of at least one compound that is the product of condensation of a succinic acid or anhydride with at least one amine, polyamine, fatty acid, (poly)oxyalkylated fatty acid, alcohol, (poly)oxyalkylated alcohol and the mixtures of these compounds. Preferably, the product of condensation of at least one succinic anhydride with at least one polyamine is used. The succinic acid or anhydride is advantageously substituted by a hydrocarbon radical which is preferably a polymeric radical, for example a polyisobutyl radical.

Preferably, said additive composition will contain from 15 to 85 wt.% of at least one polyol ester and from 85 to 15% of at least one condensation product. More preferably, it will comprise from 20 to 50 wt.% of at least one polyol ester and from 50 to 80% of at least one condensation product. Said additive composition can also contain an alcohol as described previously.

The additive composition according to the invention can also contain one or more of the additives or agents as described previously as being suitable for incorporation in the emulsified fuel according to the invention, such as for example, but nonlimitatively, one or more other emulsifying agents, one or more biocidal agents, one or more antigelling agents, one or more antisoot agents, one or more cetane number improvers, one or more filterability additives, one or more antifoaming additives, one or more detergent and/or anticorrosion additives, one or more lubricant or antiwear additives, one or more cloud point additives, one or more antisedimentation additives, one or more polyfunctional additives for cold operation. Preferably,

the additive composition contains at least one cetane number improver selected from the inorganic or organic nitrates (for example alkyl nitrates), organic peroxides and mixtures of these two types of compounds.

Thus, a particularly preferred additive composition contains at least four types of additives: at least one first ester, at least one second ester, at least one alcohol and/or one condensation product and at least one cetane number improver, each of these additives being as described previously.

According to a first embodiment, the additive composition is in the form of a mixture of the additives described previously.

According to a second embodiment, the additive composition is in the form of a "mother solution", i.e. a concentrated solution of said additives in a suitable solvent. Said solution is prepared by dissolving the emulsifying additives and any other additives and/or agents in the solvent. Said solvent can be selected from the aromatic solvents (and notably the solvents based on aromatic or naphtheno-aromatic hydrocarbons, such as for example but nonlimitatively toluene, xylenes, diisopropylbenzene or alternatively a petroleum fraction rich in aromatic hydrocarbons), petroleum fractions (in particular naphthas, gasolines, kerosenes, distillates), mineral and/or synthetic oils. The "mother solutions" can contain for example from 20 to 80 wt.% and preferably from 40 to 70 wt.% of additives and agents.

The invention finally relates to a method of improving the thermal stability of a water/liquid hydrocarbons emulsified fuel, by using a composition of emulsifying additives as described previously.

Unless stated otherwise, the ppm values are by weight.

The examples given below are intended to illustrate the invention, without limiting its scope.

Example 1:

In the present example and those that follow, a conventional gas oil G is used, complying with standard EN 590. This gas oil has the following characteristics:

Distillation range (standard ASTM D86):

initial boiling point: 177.5°C

10 vol.% point: 209.5°C

50 vol.% point: 270.5°C

90 vol.% point: 330.5°C

final boiling point: 351.7°C

Sulfur content (standard ASTM D5453): 335 ppm

Density at 15°C (standard NF EN ISO 12185): 0.8444 kg/m^3

Aniline point (standard NF M 07-021): 63.4°C

Cloud point (standard NF EN 23015): -8°C

Filterability temperature limit (standard NF EN 116): -8°C

Pour point (standard NF T 60105): -15°C

Starting with gas oil G, emulsified fuels E1 and E2, respectively, were prepared by emulsifying 87.64 wt.% of said gas oil with 10 wt.% of water, in the presence of 1.86 wt.% of an emulsifying system S and 0.5 wt.% of a cetane number improver (2-ethylhexyl nitrate).

The emulsified fuel E1 complies with the prior art, and its emulsifying system S1 is made up of:

3 parts by weight of sorbitan monooleate;

2 parts by weight of fatty acid ethoxylated at 6 mol of ethylene oxide per mole of acid;

1 part by weight of isotridecanol ethoxylated at 7.5 mol of ethylene oxide per mole of alcohol.

Fuel E2 complies with the invention, and its emulsifying system S2 is made up of:

1 part by weight of a first ester which is sorbitan monooleate;

1 part by weight of a second ester constituted of colza oil ethoxylated at 30 mol of ethylene oxide per mol of triglyceride.

Test 1:

The stability of the emulsified fuels E1 and E2 was determined at room temperature, in accordance with the stability test by centrifugation described in standard NF M 07-101. The diagram given in Figure 1 below shows the results obtained, as the degree of sedimentation of the fuel (i.e. separation of the emulsion into phases) as a function of the centrifugation time. The higher the degree of sedimentation, the lower the stability of the emulsion.

The results presented in Figure 1 clearly show the beneficial effect, in terms of emulsion stability at room temperature, of the emulsifying system S2 according to the invention: fuel E2 displays markedly better stability than the reference fuel E1.

Test 2:

Fuels E1 and E2 were also submitted to a test of stability in storage at high temperature (75°C). This test was carried out as follows: Put 450 ml of emulsion in a sealed 500-ml bottle. Put this bottle in a stove at 75°C. Then investigate the progressive phase separation by measuring the heights of the phases at time intervals of 24 h. The phase separation time is reached when the heights of the phases no longer vary with time (stationary state).

Table 1 given below shows the results obtained, as phase separation time (i.e. the time after which the aqueous and organic phases of the emulsified fuel are completely separated).

Fuel	Phase separation time (days)
E1	6
E2	9

Table 1

The above results show the considerable benefit provided by the present invention in terms of high-

temperature stability of the emulsified fuels: use of emulsifying system S2 according to the invention gives a 50% increase in the phase separation time at 75°C.

Thus, the emulsified fuels according to the invention display markedly increased stability in high-temperature storage, while maintaining excellent room-temperature stability, better than that of the emulsified fuels known in the prior art.

Example 2:

Test 2 of Example 1 (thermal stability at 75°C) was repeated, using emulsifying systems containing the same two esters as S2 (ester A = sorbitan monooleate; ester B = colza oil ethoxylated at 30 mol of ethylene oxide per mole of triglyceride), but varying the respective proportions of the two esters.

The emulsified fuels were prepared by emulsifying 87.64 wt.% of gas oil G of Example 1 with 10 wt.% of water, in the presence of 1.86 wt.% of emulsifying system S and 0.5 wt.% of a cetane number improver (2-ethylhexyl nitrate).

Table 2 given below shows the results obtained.

Sample	Composition of the emulsifying system (wt.%)		Phase separation time (days)
	ester A	ester B	
S3	75	25	3
S2	50	50	9
S4	90	10	1

Table 2

The above results illustrate the importance of the respective proportions of the two esters in the emulsified fuels and the compositions of emulsifying additives according to the invention. With the emulsifying systems S2 and S3 according to the invention, for which the weight ratios of first ester/second ester are between 20/80 and 80/20, the

thermal stability at 75°C is very much higher than that obtained with system S4.

The best results are obtained with system S2, in which the contents by weight of the two esters are equal.

Example 3:

Test 2 of Example 1 (thermal stability at 75°C) was repeated, using emulsifying systems according to the invention, containing the following two esters:

ester A': sorbitan sesquioleate;

ester B': colza oil ethoxylated at 10 mol ethylene oxide per mole of triglyceride.

The emulsified fuels were prepared by emulsifying 86 wt.% of gas oil G of Example 1 with 11.70 wt.% of water treated by osmosis, in the presence of 2 wt.% of emulsifying system S and 0.3 wt.% of a cetane number improver (2-ethylhexyl nitrate).

Table 3 given below shows the results obtained.

Sample	Composition of the emulsifying system (wt.%)		Phase separation time (days)
	ester A'	ester B'	
S5	50	50	5
S6	70	30	5

Table 3

Compared with the previous examples, this example shows that it is possible, within the scope of the present invention, to vary both the chemical nature and the respective contents of the two esters, as a function of the results that one wishes to obtain and taking into account the available products, their costs and their compatibility with other additives that are likely to be incorporated in the emulsified fuel.

Example 4:

Compositions of emulsifying additives according to the invention were prepared, using emulsifying system S2 of Example 1 (ester A = sorbitan monooleate, ester B =

colza oil ethoxylated at 30 mol ethylene oxide per mole of triglyceride, 50/50), alone or mixed with a saturated branched alcohol, namely 2-ethylhexanol.

Emulsified fuels according to the invention were prepared starting from these additive compositions by emulsifying 85.4 to 86 wt.% (depending on the tests) of gas oil G of Example 1 with 11.7 wt.% of water, 2 to 2.6 wt.% (depending on the tests) of emulsifying system S and 0.3 wt.% of a cetane number improver (2-ethylhexyl nitrate). The precise content of gas oil G in the emulsified fuel is adjusted, for each test, taking into account the amount of emulsifying system S.

Three tests were carried out, during which the composition of emulsifying system S was varied.

The stability of these fuels was determined at room temperature (25°C), using a test performed as follows: 100 ml of emulsion were put in a finely graduated Erlenmeyer flask. After the emulsion had been stored at 25°C for 24 hours, the content by volume of sedimented phase in the emulsion (the sedimented phase was constituted of large drops of aqueous phase that separated from the emulsion and coalesced at the bottom of the vessel) was determined (by direct reading on the graduated flask).

The results obtained are summarized in Table 4:

Fuel	content of ester A in the fuel (wt.%)	content of ester B in the fuel (wt.%)	content of alcohol in the fuel (wt.%)	Sedimented phase (vol.%)
E7	1	1	0	2
E8	1	1	0.4	1.5
E9	1	1	0.6	0

Table 4

The above results illustrate the additional gain in stability provided by incorporating a saturated branched alcohol in the compositions of emulsifying additives according to the invention.

In this case the compositions of emulsifying additives used in the respective fuels E8 and E9 which contain, in addition to the said first and second esters, 2-ethylhexanol display better resistance to sedimentation: on adding 0.4 wt.% of alcohol, it lowers the sedimentation of the emulsified fuel at 25°C by 25%, and on adding 0.6 wt.% of alcohol, this phenomenon of sedimentation disappears completely.

Example 5:

Test 2 of Example 1 (thermal stability at 75°C) was repeated, using emulsifying systems according to the invention, containing the following two surfactants:

ester B: colza oil ethoxylated at 30 mol ethylene oxide per mole of triglyceride.

Surfactant C: product of condensation of a polyisobutene succinic anhydride with a tetraethylenepentamine in a mass ratio amine to anhydride/amine of 1.2.

The emulsified fuels were prepared by emulsifying 86.75 wt.% of gas oil G of Example 1 with 11.70 wt.% of water treated by osmosis, in the presence of 1.25 wt.% of emulsifying system S and 0.3 wt.% of a cetane number improver (2-ethylhexyl nitrate).

The results obtained are shown in Table 5 below.

Sample	Composition of the emulsifying system (wt.%)		Phase separation time (days)
	ester B	surfactant C	
S7	30	70	15
S8	40	60	24
S9	50	50	18

Table 5

Compared with the previous examples, this example shows that it is possible, within the scope of the present invention, to vary both the chemical nature and the respective contents of the two surfactants, as a

function of the results that one wishes to obtain and taking into account the available products, their costs and their compatibility with other additives that are likely to be incorporated in the emulsified fuel.

Example 6:

Test 2 of Example 1 (thermal stability at 75°C) was repeated, using emulsifying systems according to the invention, containing the following three surfactants:

ester A: sorbitan monooleate;

ester B: colza oil ethoxylated at 30 mol ethylene oxide per mole of triglyceride.

Surfactant C: product of condensation of a polyisobutene succinic anhydride with a tetraethylenepentamine in a mass ratio amine to anhydride/amine of 1.2.

The emulsified fuels were prepared by emulsifying 86.75 wt.% of gas oil G of Example 1 with 11.70 wt.% of water treated by osmosis, in the presence of 1.25 wt.% of emulsifying system S and 0.3 wt.% of a cetane number improver (2-ethylhexyl nitrate).

The results obtained are shown in Table 6 below.

Sample	Composition of the emulsifying system (wt.%)			Phase separation time (days)
	ester A	ester B	surfactant C	
S10	20	20	60	17
S11	10	30	60	10

Table 6

Compared with the previous examples, this example shows that it is possible, within the scope of the present invention, to vary both the chemical nature and the respective contents of the two esters, as a function of the results that one wishes to obtain and taking into account the available products, their costs and their compatibility with other additives that are likely to be incorporated in the emulsified fuel.

Example 7:

Compositions of emulsifying additives according to the invention were prepared using either emulsifying system S8 of Example 5 (ester A = sorbitan monooleate, ester B = colza oil ethoxylated at 30 mol of ethylene oxide per mole of triglyceride), mixed with a saturated branched alcohol, namely 2-ethylhexanol; or the emulsifying system S10 of Example 6 (ester A = sorbitan monooleate, ester B = colza oil ethoxylated at 30 mol ethylene oxide per mole of triglyceride, surfactant C = product of condensation of a polyisobutene succinic anhydride with a tetraethylenepentamine in a mass ratio amine to anhydride of 1.2) mixed with a saturated branched alcohol, namely 2-ethylhexanol.

Emulsified fuels according to the invention were prepared starting from these additive compositions by emulsifying 85.4 to 86 wt.% (depending on the tests) of gas oil G of Example 1 with 11.7 wt.% of water, 2.5 wt.% (depending on the tests) of emulsifying system S and 0.3 wt.% of a cetane number improver (2-ethylhexyl nitrate). The exact content of gas oil G in the emulsified fuel was adjusted, for each test, taking into account the amount of emulsifying system S.

Four tests were carried out, during which the composition of emulsifying system S was varied.

The stability of these fuels was determined at room temperature (25°C), by means of a test performed as follows: 100 ml of emulsion is put in a finely graduated Erlenmeyer flask. After the emulsion had been stored at 25°C for 24 hours, the content by volume of the sedimented phase in the emulsion (the sedimented phase being constituted of large drops of aqueous phase that separated from the emulsion and coalesced at the bottom of the vessel) was determined (by direct reading on the graduated flask).

The results obtained are summarized in Table 7 below:

Fuel	content of the following in the emulsifying system:				Sedimented phase in the final emulsion (vol.%)
	ester A (wt.%)	ester B (wt.%)	surfactant C (wt.%)	alcohol (wt.%)	
S10	20	20	60	0	2
S12	14.25	14.25	43	28.5	0
S8	0	40	60	0	1.5
S13	0	28.5	43	28.5	0

TABLE 7

The above results illustrate the additional increase in stability provided by incorporating a saturated branched alcohol in the compositions of emulsifying additives according to the invention.

In this case, the respective emulsifying systems S12 and S13 contain, in addition to the first stated; second esters and third surfactant, 2-ethylhexanol, display better resistance to sedimentation: on adding 28.5 wt.% of alcohol, the phenomenon of sedimentation disappears completely.

Example 8:

Test 2 of Example 1 (thermal stability at 75°C) was repeated, using emulsifying systems according to the invention, containing the following two surfactants:

ester B": dioleate of polyethylene glycol 400 or polyalkoxylated ethylene glycol 400.

Surfactant C product of condensation of a succinic acid or anhydride with a polyamine.

The emulsified fuels were prepared by emulsifying 86.75 wt.% of gas oil G of Example 1 with 11.70 wt.% of water treated by osmosis, in the presence of 1.25 wt.% of emulsifying system S and 0.3 wt.% of a cetane number improver (2-ethylhexyl nitrate).

The results obtained are shown in Table 8 below.

Sample	Composition of the emulsifying system (wt.%)		Phase separation time (days)
	ester B"	surfactant C	
S14	20	80	20
S15	30	70	15

TABLE 8

Compared with the previous examples, this example shows that it is possible, within the scope of the present invention, to vary both the chemical nature and the respective contents of the two surfactants, as a function of the results that one wishes to obtain and taking into account the available products, their costs and their compatibility with other additives that are likely to be incorporated in the emulsified fuel.